FINAL REPORT

Microencapsulation of Biocides for Reduced Copper, Long-life Antifouling Coatings

ESTCP Project WP-0306

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14. ABSTRACT

Biofouling on ships causes deleterious effects such as increased drag. Controlling biofouling on ships is generally accomplished with biocide-based antifouling (AF) coating. As more restrictive environmental regulations are introduced and as more rigorous service life demands emerge, the need for a "next generation" environmentally friendly coating system continues to increase. Sustained and long-term biocide release is critical to AF coating performance. Microencapsulation of biocides results in increased biocide loading capacity in coatings and in reduced and controlled biocide release rates. The biocide 4,5-dichloro-2-n-octyl-4-isothi azolin-3-one (DCOIT) has been microencapsulated and incorporated into commercially relevant AF coatings. Results demonstrate long term coating system efficacy including excellent physical and antifouling performance, and a reduction of and greater control of DCOIT release rates. Controlled release technology in the form of microencapsulation has the potential to fill the performance gap that currently exists between the current and next generation of AF coating systems for the Department of Defense.

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Preface

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Abstract

Biofouling on ships causes deleterious effects such as increased drag leading to reduced speed and increased fuel consumption. Controlling biofouling on ships is generally accomplished with biocide-based antifouling (AF) coating systems. As more restrictive environmental regulations are introduced (reduce or eliminate need for cuprous oxide) and as more rigorous service life demands emerge (extend drydocking intervals), the need for a “next generation” long-life environmentally friendly coating system continues to increase. Sustained and long-term biocide release is critical to effective AF coating performance. Microencapsulation of biocides results in increased biocide loading capacity in coatings as well as reduced and controlled biocide release rates. The biocide 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) has been microencapsulated and incorporated into commercially relevant AF coating systems. Results demonstrate long term coating system efficacy including excellent physical and antifouling performance, and a reduction of and greater control of DCOIT release rates. Controlled release technology in the form of microencapsulation has the potential to fill the performance gap that currently exists between the current and next generation of AF coating systems for the Department of Defense.

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List of Acronyms

ASTM – American Society of Testing and Materials International
AF – antifouling
AI – active ingredient
AUF - amino urea formaldehyde
DCOIT – 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one
DoD – Department of Defense
EPA – Environmental Protection Agency
ESTCP – Environmental Security Technology Certification Program
HAP – hazardous air pollutant
IMO - International Maritime Organization
LOD – limit of detection
LOQ – limit of quantitation
MANTECH – manufacturing technology
MARAD – Maritime Auxiliary fleet
MPCD – Marine Pollution Control Device

MSC – Military Sea Lift Command
NEHC - Naval Environmental Health Center
ONR – Office of Naval Research
PVA – polyvinyl alcohol
QPL – qualified products list
TBT – tributyltin (also organotin)
TSCA - Toxic Substance Control Act
UNDS - Uniform National Discharge Standards
US – United States
VOC – volatile organic content

Units and Measurement Conventions

cP - centepoise
kg – kilograms
µg cm^{-2} d^{-1} – micrograms per square centimeter per day
wt% – weight percent

1 Introduction

1.1 Background

Accumulations of biofouling organisms on ship hulls increase drag and therefore negatively impact ship mission, fuel consumption, and range (Leer-Anderson and Larsson, 2003; Haslbeck and Bohlander, 1992). The battle against the deleterious effects of biofouling is, for the most part, fought with a combination of antifouling or fouling release coating systems and hull maintenance efforts such as inspections and in-water hull cleaning. Antifouling coatings are designed to release biocides over time at a rate sufficient to prevent settlement of biofouling organisms. The two most widely used types of biocide-based AF coatings on the market today are commonly referred to as ablative and self-polishing. The organic matrices slowly dissolve or react with seawater to render components of the outermost layer of the coating subject to dissolution or hydrolysis in order to avoid the buildup of long diffusion pathways. Modern antifouling coatings, therefore, release biocides via diffusion mechanisms, and are designed to erode or polish with time to ensure long service lives (Yebra et. al., 2004).

Fouling release coatings are a non-toxic class of commercially viable fouling control coatings that are characterized by elastomeric, smooth, low surface energy surfaces, the combination of which minimizes the adhesion strength between biofouling organisms and the ship hull. Organisms tend to settle during static periods and are essentially "washed away" during underway periods (Candries et al., 2000). The fast ferry and cruise ship industries have found success with these materials, but concerns remain regarding maintenance, toughness, sustained self-cleaning performance, and cost – especially for slower moving vessels of vessels that spend extended periods in port.

The most commonly used and arguably the most effective fouling control coatings are biocide-based AF coatings. Most commercial AF coating systems are designed for a 3-5 year service life. The US Navy has extended the time between drydockings of its approved systems to 10-12 years through a combination of in-water hull cleaning and hull husbandry, and by applying an extra coat of paint in anticipation of the paint thickness loss over time.

Since the 1990's, and under various funding initiatives, the incorporation of microencapsulated rapidly biodegradable organic biocides into AF coating systems has been explored. Although not yet commercialized, incorporation of microencapsulated biocides in AF coating systems results in more controlled, lower biocide release over longer periods of time than is possible with unencapsulated biocides (Haslbeck, 2004; Reybuck et al, 2006). This results in improved, extended, and environmentally friendly AF coating system performance. The majority of work in microencapsulation for AF end use applications has focused on the biocide DCOIT manufactured by Rohm and Haas (NOTE: this biocide is commonly referred to as SeaNine or SeaNine 211™. SeaNine 211™ is a 25% solution of DCOIT in xylene). These capsules have been successfully incorporated into three commercially viable antifouling coating systems produced by Jotun A/S (ablative, self-polishing, and hybrid chemistries). Results from

previously funded efforts and demonstrations indicated the advantages of microencapsulation. Critical performance demonstrations have included (see also section 2.2):

- release control in cured paint films – low and near zero order release from AF coatings compared to unencapsulated biocide
- higher active ingredient loading capacity in coating system
- compatibility with commercial coating systems
    - liquid coatings
        - low or no viscosity increase
        - no capsule agglomeration upon incorporation of capsules into liquid paint
    - dried coating films
        - no impact on cracking tendency
        - no negative impact on polishing rate
        - no impact on sprayability
- field performance
    - excellent physical and biofouling control performance (3-year evaluation)

1.2 Objectives of the Demonstration

The original objective of the WP-0306 ESTCP commercialization effort was to bring to market a fully functioning AF controlled release coating system based on the microencapsulation technology mentioned in section 1.1. To minimize risk of scale up reproducibility, a 2-phase effort was planned: a) up to 5 10kg batches with demonstration of reproducibility and stable capsule properties – risk reduction step, b) 1-2 300-500kg batches with limited demonstration of reproducibility. Scale up would be followed by a longer-term demonstration of sustained, reduced biocide release. At the same time panel and patch or whole-hull demonstration on a DoD vessel would be conducted in order to meet the requirements of the Navy's performance specification for antifouling hull coating systems, MIL-PRF 24647D (Document Center, 2006). The commercial partners were Microtek Laboratories, Inc. (microcapsule producer) working under the guidance of MACH I, Inc. and Jotun A/S (commercial paint manufacturer).

However, the original FY03 ESTCP commercialization project ended prematurely due to an unexpected field test result from a previous 3-year field test effort (ONR MANTECH funding). Analysis of aged panels had revealed that there appeared to be less DCOIT biocide remaining in coatings containing microencapsulated DCOIT compared to the coatings that contained unencapsulated DCOIT (equal weight percent initial loading of biocide). In addition, the quantity of copper remaining in the aged coatings was much lower than expected. These results could not readily be explained. The outcome of this test was brought to the attention of the ESTCP program office. The multi-year commercialization effort was terminated for lack of technical maturity. However, the ESTCP Program Office allowed the already-awarded FY03 funds to be spent out in order to fill data gaps. In addition to the original FY03 funding, ESTCP also provided $48K for long-term release rate testing, and later provided an additional $30K of funding for technical oversight. With these funds the commercial partners, now also including for the first time Rohm and Haas (providing in-kind analytical support), planned a 12-18 month effort comprising the following goals/tasks:

1) Identify and re-define key performance parameters of microencapsulated DCOIT and coatings containing those capsules to ensure focus on capsule/coating combinations suitable for effective performance as well as commercial viability.
2) Understand biocide loss over time under field exposure conditions in an effort to explain the unexpected results of the 3-year test mentioned above. Use these data to again validate effective field performance.
3) Understand how modifications to capsule properties affect biocide release rate from capsules, and then from capsule-containing coatings.
4) Demonstrate sustained, low, and constant controlled release over longer periods of time with laboratory release rate analysis of capsules in Jotun AF coatings.

The post-2003 work took longer than expected to complete. However, this has afforded us the opportunity to learn much more than we could have in a 12-month effort. The results of these efforts are summarized in this report.

Details of some methods, protocols, and processes are considered company proprietary by Jotun, Microtek, and Rohm and Haas and are not presented here. Note that Rohm and Haas received no compensation for their contributions to this effort.

1.3 Regulatory Drivers

The global and national regulatory environment continues to drive the development of more environmentally friendly fouling control coating systems.

- The recent IMO Organotin Convention (October, 2001) has essentially resulted in a global ban on the use of the biocide organotin. This has led to regional legislation (e.g. In Europe, an amendment to Marketing and Use Directive 76/769/EEC) and voluntary removal of tin-containing products from the marketplace. Although the US Navy only used TBT-based AF coatings on an experimental basis and was not directly impacted by the TBT ban, the global discussion this Convention has focused even more attention on the use of biocides in antifouling coatings in general, especially cuprous oxide.
- More strict air quality, water quality, and worker safety regulations continue to impact daily operations in shipyards and maintenance facilities. For example, in certain harbors in-water hull cleanings have been banned, and in other areas air quality regulations impact material selection and drydock/facility logistics.
- Hull coating leachate was identified as a discharge of concern from DoD vessels under the Uniform National Discharge Standards effort. Under UNDS, the DoD is working closely with the EPA and the states to identify an appropriate marine pollution control device for this discharge. The MPCD will probably take the form of a release rate limit, and will apply to all DoD vessels operating in US waters.

1.4 Stakeholder/End-User Issues

NAVSEA Code 05M1 is the Technical Warrant Holder for corrosion and coatings. Code 05M1 has taken a lead role in identifying and transitioning next generation fouling control coating systems into the fleet. The goal is to replace the current copper ablative coatings with copper-free or reduced copper ablative or self-polishing coatings, or non-toxic fouling release

coating systems, or both. Expectations are high for sustained performance and environmental targets (adapted from M. Ingle, 2006).

- Reduce or eliminate copper
  - Biocide based – self-polishing or ablative technology in the form of
    - Reduced copper release rate coatings OR
    - Copper-free coatings OR
    - Rapidly biodegradable biocide based coatings – single biocides or combinations
  - Non-biocide based - low surface energy fouling release non-toxic coatings
- Achieve extended service life to support 12-year drydocking cycles
  - Without need for in-water hull cleaning
  - At reduced logistics and maintenance cost
- Comply with environmental regulations
  - VOC
  - HAP
  - EPA registration
  - NEHC approval
- Require practical coating application equipment and standard personal protection equipment for applicators
- Meet or exceed performance specification requirements (MIL-PRF-24647D)

For the last 5-6 years the NAVSEA 05M1 has sponsored a robust program to identify and qualify coating systems that meet or exceed the above criteria (NST Center, 2006). More than two dozen materials have been assessed, and none have met the suite of established criteria. Coating technologies based on microencapsulated biocides fit well within the established criteria. Controlled release technology has the potential to fill the performance gap that currently exists.

Army, Marine Corps, US Coast Guard, MARAD, and MSC often take advantage of Navy qualified materials for use on service vessels, and must answer to the same national and regional environmental regulations. Therefore multiple DoD agencies would directly benefit from the successful implementation of improved, environmentally compliant, long-lasting antifouling coating systems based on microencapsulation technology.

2 Technology Description

2.1 Technology Development and Application

The technology of microencapsulation is widely used and well-developed for pharmaceutical and agricultural applications. Among the most common applications for microencapsulation are time-release medications, extended-release fertilizers, and carbonless paper, but the possibilities for uses are endless. Its use to control biocide release from antifouling coatings is a new application of the technology.

The process of encapsulation involves the deposition of a polymeric wall material around a central core or active ingredient. For many encapsulation techniques, the wall and core materials are immiscible resulting in an oil-in-water or water-in-oil emulsion. Reactants polymerize at the interface under controlled reaction conditions to form the capsule wall. The wall material is often later crosslinked, and the final product filtered and dried to a free-flowing powder.

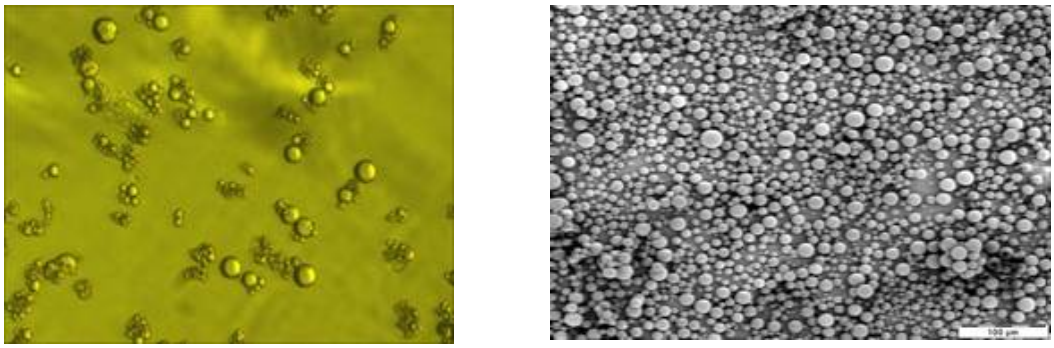

Figure 1. Typical microcapsules. Diameters from 5-45 microns. (L) Capsule in solvent slurry. (R) Optimized dried powder of microcapsules. No drying agent required; few agglomerates.

Potential release mechanisms are many, ranging from "rapid on demand" release such as breakage of the capsule wall to "very slow" such as diffusion controlled release. In our case, release of the core biocide is through a simple diffusion process. Adjustments to parameters such as wall material, wall thickness, crosslinking, capsule diameter, core loading and loading of microcapsules in the paint, impacts the eventual rate of biocide release from the capsules and from the coating containing the capsules (Fig. 1).

2.2 Previous Testing of the Technology

Prior research, most recently funded by the ONR MANTECH office, demonstrated that the formulation of microencapsulated DCOIT into ablative or self-polishing coatings systems resulted in a controlled release rate, extended performance life, and improved AF performance (Haslbeck, 2004).

Microcapsules were produced in up to 1 kg batches, ranged from 30-60 microns in diameter, and contained 40 weight percent of AI. They were loaded at 1, 2, and 3 weight percent AI into three fully-developed commercial AF coating systems of varying chemistries (ablative, self-polishing, and hybrid). Compatibility studies demonstrated the capsules and binder/resin systems co-mixed without degrading applied coating properties including storage stability, polishing rate, and cracking tendency. Some combinations of capsules and liquid binder/resin systems caused a significant increase in viscosity to the point where the coating became unsprayable after 3-4 days (Table 1). Systems that became unsprayable were not selected for follow-on testing.

After applying downselect criteria to the various capsule/coating combinations, test panels were prepared for field evaluation of antifouling performance based on established ASTM static and dynamic panel exposure and inspection methods (ASTM D3623, 2006; ASTM D4939, 2006; ASTM D6990, 2006). In addition, biocide release rates (both the copper and organic biocide) were measured based on established and draft ASTM release rate quantification methods for copper and DCOIT respectively (ASTM D6442, 2006; ASTM Z9489Z, 2006).

Comparisons of field performance, release rate, and dry film physical properties were made between unencapsulated and encapsulated booster biocides in all three coating binder/resin

Viscosity Study in Three Commercially Relevant AF Coatings Comparison of Encapsulated and Unencapsulated DCOIT at 2 w/w Loading *(viscosity reported in centipoise)*								
Product / (storage condition)	**Start**	**1 day**	**2 days**	**3 days**	**6 days**	**2 weeks**	**4 weeks**	**8 weeks**
Hybrid (L)	460	460	-	-	460	470	480	570
Hybrid (H)	460	480	-	-	490	520	440	-
Hybrid + ME (L)	450	730	760	910	>1000	>1000	>1000	>1000
Hybrid + ME (H)	450	>1000	>1000	>1000	>1000	>1000	>1000	-
Self-Polishing (L)	780	720	-	-	810	850	800	780
Self-Polishing (H)	780	660	-	-	760	820	700	-
Self-Polishing + ME (L)	700	800	830	840	930	>1000	>1000	>1000
Self-Polishing + ME (H)	700	800	760	>1000	>1000	>1000	>1000	-
Ablative (L)	330	-	-	-	-	-	340	360
Ablative (H)	280	290	-	-	360	440	400	-
Ablative + ME (L)	260	350	420	440	510	550	580	680
Ablative + ME (H)	260	490	530	450	520	500	480	-

NOTE: (H) = test conducted at high temperature (50°C); (L) = test conducted at low temperature (23°C); ME = microencapsulated

Table 1. Change in viscosity (cP) of coatings with and without encapsulated DCOIT at 23°C and 50°C. A viscosity of > 750 indicates the material is "unsprayable".

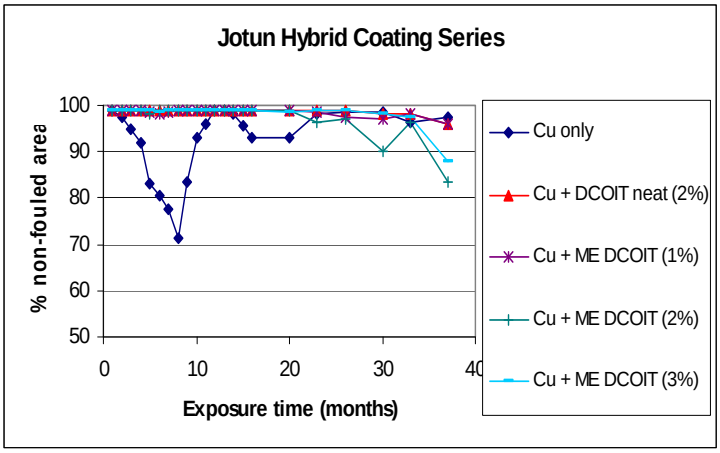

Figure 2. Biofouling accumulation over time. Capsule-containing coatings offer improved AI management, and therefore extended performance. Other coating types and capsule combinations evaluated, but data not shown.

systems. The coating systems containing encapsulated organic biocides remained free of hard fouling for 18-30 months depending on the formulation (Fig 2).

Release rate data show that microencapsulation results in highly controlled and significantly lower release of biocide from the coating system when compared to unencapsulated biocide in he same binder/resin system (Fig 3).

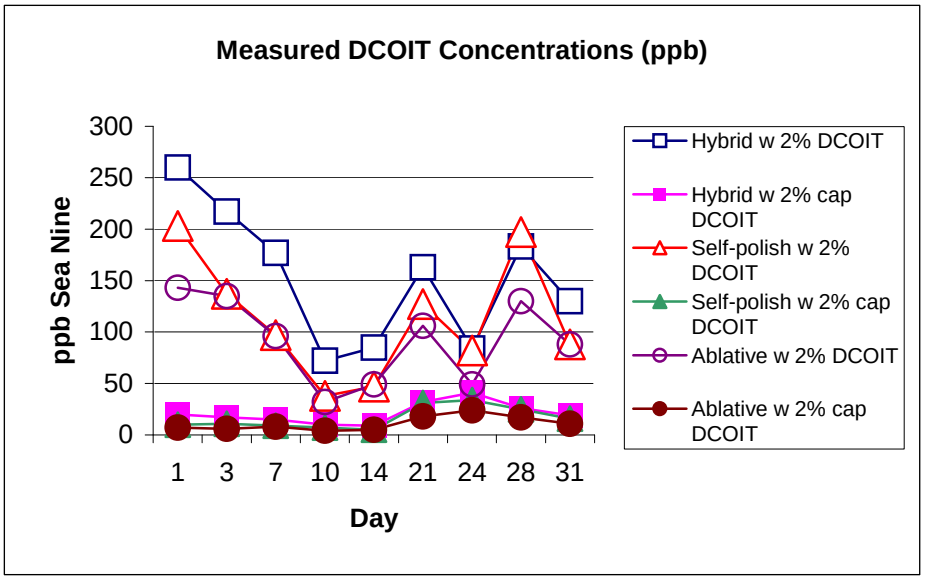

Figure 3. Comparison of release of organic biocide encapsulated vs. unencapsulated. "cap" indicates the biocide has been microencapsulated.

Results of this previously-funded work served to demonstrate the feasibility and efficacy of microencapsulation in commercial coating systems. Results indicated extended and controlled release of organic booster biocides. The work established a benchmark from which we could launch a technology scale-up and commercialization effort for controlled release, capsule-containing AF coating technology.

2.3 Projected Material Cost

Coatings containing microencapsulated biocides are expected to cost more per gallon than currently used copper ablative systems. However, this increase in cost is not expected to be significantly higher than the cost of next-generation biocide-based coating systems (especially self-polishing and fouling release systems) that meet or exceed DoD performance and environmental criteria. Because no systems of this type have been added to the Navy's QPL in recent years, there is not current cost basis on which to project a future material cost. Current QPL AF coatings typically cost approximately 40 dollars per gallon. Material cost, however, is proportionally low relative to labor costs such as surface preparation, coating application, coating removal, and maintenance.

2.4 Advantages and Limitations of the Technology

The advantages of microencapsulation over free-association incorporation of biocides into coatings include:

- Larger reservoir of biocide in coating than free association
- "Free biocide" management within coating
- Release rate control above and beyond the capabilities of ablative or self-polishing coatings alone

- May reduce skin sensitization issues for shipyard workers (during application and removal)
- Low, sustained, effective release of encapsulated biocide which may make up for reductions in copper release rates over long periods of time (NOTE: DCOIT is effective against not only slime organisms, but also barnacle fouling).
- Diffusion properties customizable through systematic wall property and core modifications

Limitations of microencapsulation technology include:

- Increased coating cost
- Incorporation of microencapsulated DCOIT may result in the requirement to re-register the biocide and the coatings that contain it with EPA.

3 Demonstration Plan

3.1 Performance Objectives

Successful performance of antifouling coating systems for the US Navy are outlined in the performance specification MIL-PRF-24647D (Document Library, 2006) (Figure 4).

3.2 Selecting Test Platforms/Facilities

A typical suite of QPL qualification tests consists of static panel testing, ship patch testing, whole ship or quarter hull testing, and any required evaluations for EPA registration (for biocide-based coating systems).

3.3 Test Platform/Facility Characteristics/History

MACH I, Inc. – working together with Microtek produce microencapsulated DCOIT. Laboratory facilities equipped to produce from 100g – 500kg batches of microcapsules. These companies produce commercially relevant microcapsules for a wide array of end use applications.

Rohm and Haas Company – world class producer of DCOIT and of other biocides and commercially relevant chemicals and products. High capacity production facilities.

Jotun A/S – one of the top 5 antifouling coating manufacturers worldwide. Headquartered in Norway. High capacity production facilities in various countries, including the USA.

Panel testing sites -

- NRL Key West – test panel preparation (Kew West site) and field evaluation site (at Coast Guard facility in Biscayne Bay, Miami, FL) for qualification of commercially viable antifouling coating systems. NRL Key West Typically used by NAVSEA 05M1 for required QPL panel testing.
- Battelle Memorial Laboratory, Daytona Beach, FL – commercial test site
- Miami Marine Research and Testing Station, Riviera Beach, FL – commercial test site.

Patch and ship platforms - MSC, Coast Guard, US Navy fleet – routinely provide platforms for NAVSEA 05M1-sponsored coating system demonstration efforts. All ship patch and whole hull evaluations are coordinated through NAVSEA Code 05M1.

3.4 Present Operations

The current suite of QPL antifouling coating systems has been in place for well over a decade. They are cuprous oxide based ablative antifouling coating systems which meet or exceed the performance requirements outlined in the performance specification. The needs for future coating systems are outlined in section 1.4. The most critical criteria for emerging coating systems include: extended performance life with little or no requirement for in-water hull cleaning, meet or exceed current and emerging environmental restrictions including, but not limited to, a reduction or elimination of copper release.

3.5 Pre-Demonstration Testing and Analysis

Section 2.2 outlines results from prior efforts with capsules and capsule-containing coatings. With respect to biofouling control, historical data suggests that capsule-containing coatings perform equally as well if not better than current QPL coating systems in field tests, although they have not to date been evaluated side by side. In addition, with respect to DCOIT release rate control, historical data demonstrates that capsule-containing coating systems significantly reduce and regulate biocide release rate over unencapsulated DCOIT. And, capsule-containing coatings can be loaded with a greater quantity of biocide than possible with unencapsulated DCOIT. Together, these facts strongly indicate extended efficacy and performance of capsule-containing coating systems.

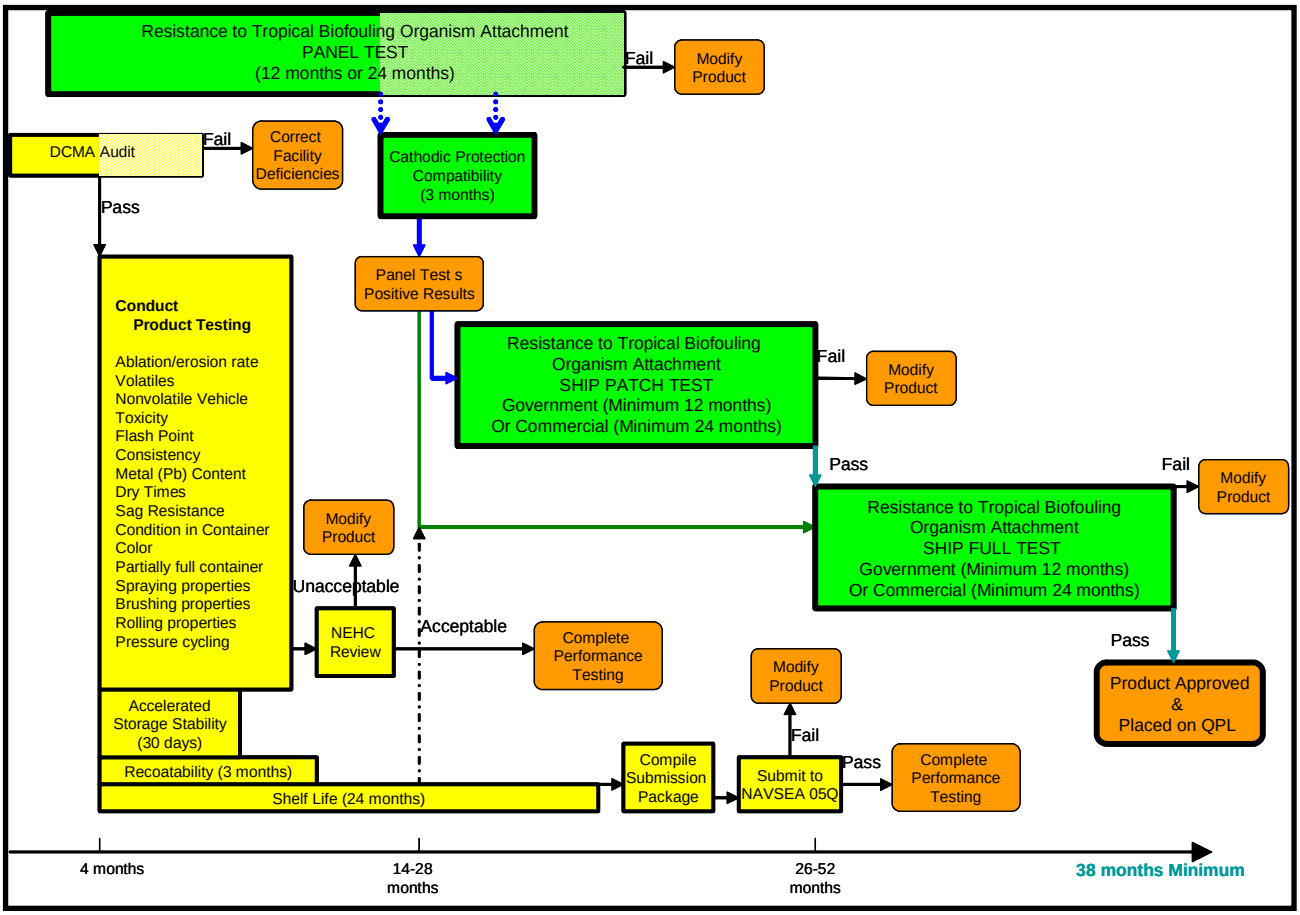

Figure 4. Approximate testing and evaluation requirements of AF coating system in accordance with MIL-PRF-24647D; assumes continuous interaction and dialogue with Technical Warrant Holder. (D. Fayocavitz, 2006)

3.6 Testing and Evaluation Plan

As outlined in Section 1.2 above, the FY03 ESTCP commercialization project ended prematurely due to an unexpected set of results from a previous 3-year field test effort (ONR MANTECH funding) that could not be readily explained. A plan was devised, therefore, to spend out the remaining funds. All parties agreed that the main thrust of our efforts should target both an improved understanding of how capsule formulation modifications impact diffusion, and of the mechanics of diffusion/release of biocide from capsules and from capsules in coatings. The following tasks were proposed to achieve the overarching goals.

1) identify and re-define key performance parameters of microencapsulated DCOIT and coatings containing those capsules to ensure focus on capsule/coating combinations suitable for effective performance as well as commercial viability.
2) understand biocide loss over time under field exposure conditions in an effort to explain the unexpected results of the 3-year test mentioned above. Use these data to again validate effective field performance.
3) understand how modifications to capsule properties affect biocide release rate from capsules, and then from capsule-containing coatings.

4) conduct release rate analysis of capsules in Jotun AF coatings to demonstrate sustained, low, and constant controlled release over long periods of time (months)

Using knowledge from 2 and 3, we would develop a better accounting for biocide diffusion mechanics from capsules through and out of the coating. A detailed description of each task is outlined in section 4.1.1 below.

4 Test and Evaluation Plan

4.1.1 Detailed Description of New Tasks

1) Key Capsule and Performance Parameters

Before moving forward on modifications to the microcapsule or coating system, key capsule parameters and key performance parameters were re-stated and more completely defined. This suite of parameters would need to be met in order to produce commercially viable microcapsule-containing AF coating systems. Processes and evaluation protocols were established for each. Capsules from previous work had essentially met the parameters listed below, yet modifications were envisioned for future batches in order to complete the ESTCP-funded studies. Therefore, it was imperative that future capsule batches produced under this task also met or exceeded the following criteria before being considered for follow-on evaluation. See "3) Capsule Property Studies" below for relevant protocols.

- Agglomeration and capsule size
  - The final capsule product must be in a free-flowing powder form, free of agglomerates and "leaky" capsules, and fully compatible with the liquid coating into which it would be formulated. NOTE: Agglomerated or leaky capsules do not produce free-flowing powders of dried capsules without the aid of a drying agent. Free-flowing is a qualitative term, and is applied by the experienced capsule manufacturer.
  - Capsule size target – average diameter less than 30 microns (later target lowered to 20 microns).
- Wall integrity
  - The final capsule product must hold up to airless spray, not degrade when formulated into the liquid coating, and not crack or break during paint film drying process.
- In-can stability
  - The final capsule must not prematurely release AI (core) to the surrounding liquid coating system between production and material application.
  - The final capsule must not negatively impact the liquid coating properties such as viscosity.
- Environmental considerations
  - The final coating system must not be subject to any international trade or environmental restrictions. It must be a fully commercially viable coating system.
    - The DCOIT (biocide) solvent for the core used in the earliest batches of microcapsules was SAS310, which is listed on the TSCA section

12.d (limited global import/export restrictions apply) (US EPA, 2006). An alternate solvent was required.
        - DCOIT is an EPA-registered biocide, and the Jotun ablative coating without microcapsules an EPA-registered marine AF coating system. The encapsulated DCOIT and the encapsulated DCOIT in a marine AF coating system may require a separate EPA registration (TBD).
        - The final system would need to meet or exceed anticipated copper release rate limits (this limit not yet published; emerging out of the UNDS effort).
- Dry coating – capsule compatibility
    - Incorporation of the capsule into the coating (dried film) must not degrade the properties of the coating system (cracking, adhesion, roughness, polishing rate).
- Commercially viable coating-capsule system
    - The final product must be commercially viable. Avoid cost-prohibitive production processes, materials, or additives
- Performance advantage
    - The final product must demonstrate a performance advantage over unencapsulated biocide, or, at a minimum, evaluation results must indicate sustained, improved performance over current QPL systems.

2) Field Exposure

In order to better understand the rate of biocide loss with time from a field-exposed coating, we designed a 12-month study to mimic the previous 3-year study. Test panels were exposed under static and dynamic (accelerated) conditions.

Biocide loss with time (quarterly sampling) was monitored by destructively sampling the aged coating films (scraping) and quantitatively analyzing for remaining biocide. Three different coatings (all based on the commercially available Jotun A/S ablative copper system) were applied to 10" x 12" flat panels and 3" x 6" curved panels for constant depth static exposure and static/dynamic exposure based on ASTM D3623 and ASTM D4939 respectively. The testing was conducted at the Battelle Memorial Laboratory test site in Daytona Beach, FL. Figure 5 shows panel exposure systems/racks (static and dynamic) at Florida test site. See Appendix A for details of panel preparation. The commercial version without capsules was included as a reference material.

Due to time limitations, we formulated these coatings with microcapsules (batch 49-34) having very similar properties as the type originally used in the 3-year field evaluation (batch M44-50) instead of waiting for more "optimized" capsules from the capsule property studies (see below). In addition, we wanted to reproduce, as much as possible, the conditions of the original study in an attempt to explain the previous results. Batch M49-34 had the following characteristics:

- Same solvent used for DCOIT (core) as in original study (SAS-310)
- Core contained 35.5 weight percent DCOIT – same as original study
- The AI loading in the coating was approximately 2%.

- Average diameter < 30 microns, but maximum diameter 140 microns. This is slightly larger than the M44-50 capsules from the original study which had an average diameter of < 30, but maximum diameter about 80 microns.
- Slightly thicker capsule wall than those used in the original study

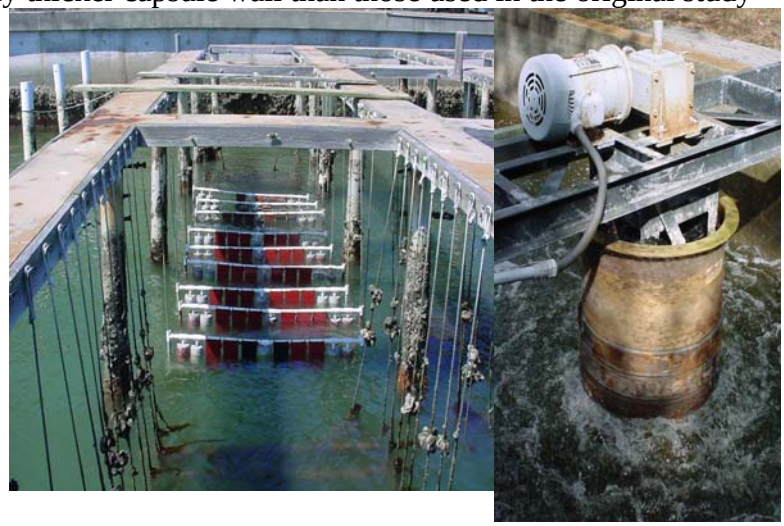

Figure 5. Florida test site. A) static panel exposure. B) dynamic panel exposure

At regular intervals, a single panel of each type was removed from the test site, dried, wrapped, and shipped to Rohm and Haas. Two methods of analysis were used to quantify remaining DCOIT in each panel. 1) A known area of the coated panel was scraped to remove all of the applied coating. The scraped coating was sonicated and extracted with acetonitrile to disrupt all of the paint and to extract the DCOIT. 2) Square sections were cut out of each panel. These were placed in vials and sonicated for 4 hours in acetonitrile to remove all of the paint from the panel and to extract the DCOIT. For both methods, further sonication and extraction with acetonitrile showed that no additional DCOIT was extracted out of the paint samples.

3) Capsule Property Studies

A systematic capsule property study was planned to gain a more comprehensive understanding of the relationship between capsule properties (size, wall thickness, wall material, core loading) and release mechanism, release rate, diffusion rates, and coating performance. The following studies were planned:

- Wall thickness – Thicker walls are known to slow core (biocide) release relative to thinner walls. Wall thickness studies were planned to better understand the impact of wall thickness using several wall chemistries. Capsule chemistry, such as ratios of PVA to phenolic components, and production conditions, such as rate of stirring, pH, and temperature, were systematically adjusted to produce capsules of various wall thickness. Capsules were dried, incorporated into a carrier (coating or resin), sectioned, and inspected microscopically (high magnification light microscopy and SEM) to quantify wall thickness.

- Reproducibility –A database of sequentially-produced identical batches of microcapsules would determine capsule property reproducibility from batch to batch. Reproducibility was assessed based on capsule core loading, wall thickness, mean diameter, and xylene extraction data (see "storage stability" below).
- Core loading – Higher core loading is desired to facilitate extended coating performance life and maximum commercial benefit. Note that pre-ESTCP Program attempts to load PVA-Phenolic capsules above approximately 40 weight percent DCOIT had been unsuccessful. Core loading is defined as the weight percent DCOIT incorporated into the capsule core (calculation based on starting materials).
- Core solvent for biocide – Pre-ESTCP Program batches of DCOIT capsules were based on a core material consisting of DCOIT dissolved in an organic solvent (SAS 310). However, encapsulation of "neat" DCOIT is the most desired approach since the requirement for a core solvent limits maximum core loading, and it would eliminate any possible TSCA 12.d restrictions referenced in 4.1.1 section 1. Barring success, alternative core solvents would be explored.
- Capsule diameter – Pre-ESTCP Program batches of capsules averaged about 30-40 µm in diameter with a range of 5-100 microns. The target was set at 20µm average diameter with a narrower size range. Capsules of more uniform diameter produce more controlled release rates, and can impact coating physical properties. A Coulter LS Particle Size Analyzer is used to quantify mean capsule diameter.
- Capsule wall material – Pre-ESTCP Program capsule batches comprised PVA-Phenolic wall chemistry. The maximum DCOIT loading achievable prior to the capsule formulation study was 40 weight percent. AUF, an alternative wall material, had used previously but not fully developed. Under this ESTCP task, we would further explore AUF wall chemistry as a means to eliminate the need for a biocide core solvent.
- Sprayability – There had been no previous evidence of capsule breakage or cracking as a result of formulation processes or airless spray application. Future batches of capsules must meet or exceed this criterion. To date, sprayability has been qualitatively assessed by passing a slurry of solvent/capsules or coating/capsules through an airless spray gun and either microscopically evaluating physical integrity of capsules (cracks), quantitatively analyzing the solvent (xylene or paint respectively) for unencapsulated DCOIT, or through a qualitative assessment of cured paint film properties. These are not standardized practices.
- Storage stability – Premature release of DCOIT from the capsules into the liquid coating is undesirable. A screening technique was devised by Rohm and Haas and adopted by Microtek to quantify DCOIT release into xylene, the most important solvent used in the Jotun antifouling coatings formulations, and one in which DCOIT is relatively highly soluble. This protocol provided a convenient means for screening the dozens of capsule batches based on xylene extraction rates (also an indicator of storage stability). Reproducibility of this method has not been quantified, and it is not a standard practice.
    - Microgram quantities of capsules were suspended in a fixed volume of xylene and held statically either at room temperature or elevated temperatures (45^{o}C).
    - Periodically aliquots were quantitatively analyzed for DCOIT.
    - Rohm and Haas also used this protocol with seawater as the solvent.

- Room temperature data were compared to elevated temperature (45^{o}C) data; the elevated temperatures accelerated DCOIT extraction from the capsules.

Capsules with low xylene extraction rates and high seawater extraction rates were desirable since those capsules would tend to retain DCOIT while in the liquid paint, and yet release it from the coating upon exposure to seawater.

- In addition, the coating must not increase in viscosity over time (> 750 cP indicates negative impact on sprayability). This parameter was evaluated on coatings produced under the ONR-MANTECH effort, but, due to budget and time restrictions, was not comprehensively applied to coatings produced under this effort.

Nearly three dozen 100-250g batches of capsules were produced for the capsule property study (Table 2). As outlined above, systematic variations in core loading, core solvent, wall thickness, capsule diameter and size distribution, and wall chemistry were made in order to better understand impact on capsule integrity, core release, wall integrity, storage stability, and capsule-coating properties.

In order to save time and conserve resources, Rohm and Haas Company developed an extraction study protocols that provided relative indications of biocide release prior to formulating capsules into coatings. Milligram quantities of capsules were suspended in milliliter volumes of solvent and the solutions were maintained under static conditions either at room temperature or at elevated temperatures over up to 112 days. At pre-detemrined intervals aliquots of the solvent were quantitatively analyzed for DCOIT. Both xylene (room temperature and high temperature (45^{o}C)) and seawater (room temperature) extraction protocols were developed. Both Rohm and Haas Company and Microtek used the protocols for screening purposes.

Xylene is the main solvent used in the antifouling coating systems of interest, and DCOIT is relatively highly soluble in xylene. Exposure to xylene, therefore, represents the most significant challenge to wall integrity. Seawater extraction gives an indication of relative biocide release under in-service conditions. Both xylene and seawater extraction rates can indicate relative diffusion rates based on wall properties, and can be indicative of leaky or compromised capsule walls. Results of these analyses were used as indicators of wall property modifications (thickness, chemistry, crosslinking), storage stability, in-service release rate, reproducibility, and durability or toughness. Capsules with relatively low xylene extraction and relatively high seawater extraction were desired since these capsules would most likely remain stable during in-can storage periods (exposed to xylene) yet release the core (biocide) during periods of seawater exposure (in service).

4) Release Rate Analysis

Upon completion of a comprehensive capsule formulation study, three batches of microcapsules were selected for long-term laboratory release rate testing. Jotun's commercial ablative coating was selected as the base coating formulation. Copper and DCOIT release rates were determined based on ASTM published copper release rate method (ASTM D6442) and a draft ASTM organic biocide release rate method (ASTM Z9489Z) respectively (ASTM, 2006(a); ASTM, 2006(b)).

These methods typically call for the application of the test coating to the external circumference of a polycarbonate cylinder (200 cm^2). The cylinders are then aged in a holding tank of artificial seawater held at constant pH, temperature, and salinity. On a sampling day, the cylinders are moved to individual release rate measurement chambers containing a fixed volume of artificial seawater where they are rotated at 60 RPM for 1 hour. Aliquots are taken from the release rate measurement chambers and quantitatively analyzed for the biocide.

The following capsule batches were selected:

- Batch M49-34 - PVA-Phenolic wall chemistry. Selected because this was the batch used in 12-month field panel study.
- Batch M56-24 - PVA-Phenolic wall chemistry. Selected because it used a non-TSCA 12.d listed solvent, had a smaller particle size than M49-39, and had a lower xylene extraction rate than M49-34.
- Batch 56-55 - AUF wall chemistry. Selected for alternative wall chemistry. Among the batches of that wall chemistry, this series had a high core loading, no core solvent, relatively thin wall, and a low xylene extraction rate

DCOIT loadings were set at 2 and 6 weight percent. The test was planned for a period of 180 days (6 months) in order to demonstrate extended and controlled release (ASTM release rate studies are typically run for a minimum of 45-days and up to 90 days). Given that this was a screening assessment, we reduced the number of sampling days to conserve resources. We also extended rotation time of the painted cylinder in the measurement tank from one to five hours in anticipation of very low DCOIT release rates such that the biocide would be present at detectable levels.

4.1.2 Results of New Tasks

1) Key Capsule and Performance Parameters

Agglomeration and capsule size:
Capsules were produced that met the key performance criteria for agglomeration and capsule size. Many batches were characterized by average diameters of less than 20 µm and a maximum capsule diameter of 30 µm (Table 2). In addition, many were successfully dried to a free-flowing powder without the use of drying aids, even when "neat" DCOIT was microencapsulated such as with amino urea formaldehyde wall chemistry (Figure 6). Capsules with poor wall integrity cannot be dried to a free-flowing powder without the use of drying aids. Poor wall integrity or "leakiness" is indicated by sustained high xylene extraction rates (see next section on wall integrity for a summary of xylene extraction studies)

Wall integrity:
Three separate analyses demonstrated the capsule wall integrity.

Airless Spray Impact on Capsules: Using commercially relevant airless spray equipment, several hundred millilitres of a Jotun copper ablative coating containing M44-50 batch capsules (produced under pre-ESTCP funded effort) were sprayed into an empty paint can at the Jotun facility and then shipped to Rohm and Haas. The elapsed time between spray and analysis was approximately 3 months.

Table 2. Capsule batches – Historical, PVA-Phenolic, and AUF.

Batch number	Core Solvent	Ratio DCOIT: Solvent in Core	Approx. DCOIT Content, wt%	Approx. Core Loading, wt%*	Mean Partice Size, µ*	Fraction < 30 microns	Comments	Xylene Extraction	Seawater Extraction	Spray Test for Wall Integrity	In-Can Stability Study	Formulated into coating	Field Exposure
Historical batches					Mean Partice Size, µ								
M44-50	SAS-310	Prior Work	35.5	N/A	< 25	56	Historical batches	Y		Y			Y*
M49-34	SAS-310	Prior Work	35.5	N/A	< 30	31.8	slightly thicker wall than M44-50	Y			Y	Y	Y**
M50-52	Prior Work	Prior Work	41	N/A	N/A	16.8	Historical batches	Y					
M50-53	Prior Work	Prior Work	41	N/A	N/A	14.7	Historical batches	Y					
M50-54	Prior Work	Prior Work	41	N/A	N/A	16.6	Historical batches	Y					
M52-71	Prior Work	Prior Work	40	N/A	N/A	61.2	Historical batches	Y					
M52-70	Prior Work	Prior Work	40	N/A	N/A	91.6	Based on base line process	Y	Y				
PVA-Phenolic batches				* = data not available								* = ONR MANTECH; **	
52-70	SAS-310	50:50	40	80	18.9	91.6	Base line process (prep 5-6-04)	Y	Y				
56-19A	SAS-310	50:50	40	80	22.4	78.9	Replic.52-70 proc., less cure	Y					
56-19B	"	"	"	"	23	75.9	Replic.52-70 proc.	Y					
56-20A	PXE	50:50	40	80	19.7	89.3	Replic.56-19A proc.	Y					
56-20B	"	"	"	"	19.8	89.2	Replic. 56-19B proc.	Y					
56-21A	C13 alkyl benzene	50:50	40	80	21.9	80.9	Replic. 56-19A proc.	Y					
56-21B	"	"	"	"	21.9	80.9	Replic. 56-19B proc.	Y					
56-22A	Exxon 100	50:50	40	80	22.9	75	Replic. 56-19A proc.	Y					
56-22B	"	"	"	"	23	74.9	Replic. 56-19B proc.	Y					
56-23	min.spirits	50:50	40	80	20.6	87.3	Replic. 56-19B proc.	Y					
56-24	mineral oil	50:50	40	80	19.5	88.7	Replic. 56-19B proc.	Y	Y			Y	
56-26	Exxon 100	50:50	40	80	23.4	74.6	Reprod 56-22B at 2x scale	Y	Y				
56-27	Exxon 100	50:50	40	80	21.8	78.9	Mod 52-70 proc. to tighten wall	Y					
56-28	Exxon 100	50:50	40	80	45	13.8	Mod 52-70 proc. to tighten wall	Y					
56-29	Exxon 100	50:50	40	80	21.9	77.5	Mod 52-70 proc. to tighten wall	Y	Y				
56-34	Exxon 100	75:25	59	80	17.6	93.7	56-22B proc.; 75% DCOIT	Y					
56-35	Exxon 100	50:50	35	70	24.6	71.9	Thicker wall, reduced core	Y	Y				
56-38A	Exxon 100	50:50	38	76	21.1	86.1	Proc. mod, thicker wall	Y					
56-38B	"	"	"	"	"	"	Proc. mod, thicker wall	Y					
56-43	Exxon 150	50:50	40	80	20.4	87.1	Replic. 56-19B proc.	Y					
56-44	Exxon 200	50:50	40	80	20.2	86.2	Replic. 56-19B proc.	Y					
56-59	Exxon 150	50:50	40	80	20.5	87.8	Replic. 56-43 proc.	Y					
56-58	Exxon 200	50:50	40	80	19.6	86.5	Replic. 56-44 proc.	Y					
Amino-Ureaformaldehyde batches													
56-40	Exxon 100	50:50	42	84	13.8	99.1	Conventional process	Y	Y				
56-41	None	-	85	85	18.6	86.7	Conventional process	Y					
56-42	None	-	81	81	18.4	87.9	Thicker wall, reduced core	Y					
56-45	None	-	85	85	19.8	85.2	Reprod. M56-41 at 2x scale	Y	Y				
56-48	None	-	80	80	13.9	98.3	Process modification	Y					
56-54	Exxon 150	85:15	72	85	13.8	99.4	Conventional process	Y					
56-55	None	-	89	89	18.7	89.9	Increased core, thinner wall	Y	Y			Y	
56-56	None	-	85	85	13.2	99.2	Process mod, less cure	Y	Y				
56-61	None	-	85	85	19.6	85.4	Process modification	Y	Y				

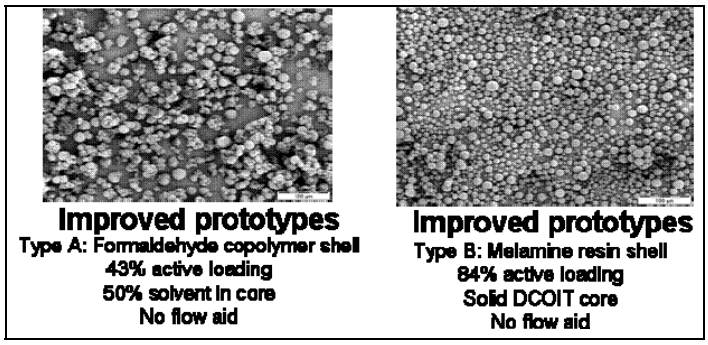

Figure 6. Images microencapsulated DCOIT. Minimal agglomeration, dry flowing powder (no drying aid), acceptable particle size and particle size distribution.

- From this sample, Rohm and Haas analyzed the liquid and dried paint (techniques proprietary) from this sample and could not detect cracking or compromised capsule integrity as a result of airless spray processes.
- Rohm and Haas also applied the liquid coating from this sample to coupons and allowed the coating to dry. Coupons were sectioned and analyzed them using sophisticated microscopy techniques (techniques proprietary). The capsule walls were deemed intact and unaffected by incorporation into the dried paint film.
  - NOTE: Rohm and Haas analyzed several other dried coating films from other on-going investigations and subjected them to the same sectioning and microscopic analyses. Again, the capsule walls were not affected by incorporation into the dried paint films (Figure 7).

- Film formation: If incorporated at high levels, neat DCOIT can cause poor film properties because it acts as a plasticizer in dried paint films. Had the capsule walls failed to contain the DCOIT in any of the samples analyzed, then poor film-forming results would have been observed.

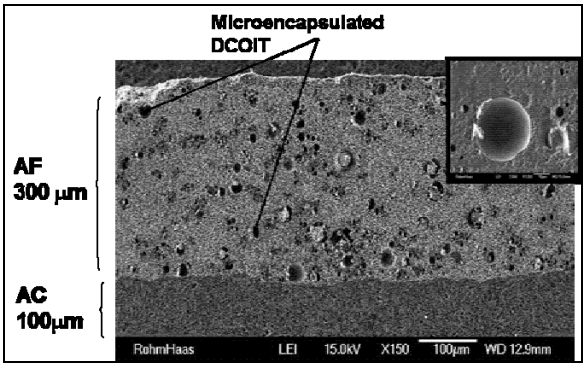

Figure 7. Cross-section of two-layer antifouling system – dried paint film. Microcapsules are well-distributed throughout film, and capsules survive airless spray application without breaking or cracking.

- Xylene and Seawater Extraction: Batches with sustained high extraction of core material into xylene such as M50-52, M52-71, M56-34, and M56-43 were characterized by compromised or poor wall integrity (Table 3).

Batch number	Comments	Day 1	Day 7	Day 14	Day 28	Day 56	Day 112
Historical batches							
M44-50	Historical batches	19.3	29.8	31.1	38.8		
M49-34	slightly thicker wall than M44-50	2.9	11.2	11.3	15.1		
M50-52	Historical batches	12.6	23.7	23.4	28.8		
M50-53	Historical batches	-	5.2	4.9	13		
"	repeat analys	2.4	4.2	3.9	7.7		
M50-54	Historical batches	2.3	3.7	1.1	2.6		
M52-71	Based on base line process	-	18.5	20.1	26.7		
"	repeat analys	11.3	18.1	18.4	25.2		
M52-70	Based on base line process	-	2.3	1.7	0.4		
"	repeat analys	0.5	1.3	-1.1	0.8		
PVA-Phenolic batches							
52-70	Base line process (prep 5-6-04)	na, 0.5	2.3, 1.3	1.7, -1.1	0.4, 0.8	1.6, 1.1	
56-19A	Replic.52-70 proc., less cure	7.3	9.9	13	16.4	na	
56-19B	Replic.52-70 proc.	1	-0.5	2.5	3.7	na	
56-20A	Replic.56-19A proc.	7.4	7.2	12.4	15.2	na	
56-20B	Replic. 56-19B proc.	-0.3	-0.2	1.5	2.3	na	
56-21A	Replic. 56-19A proc.	0.5	-0.1	3	4.4	na	
56-21B	Replic. 56-19B proc.	-0.5	-0.2	1.4	2	na	
56-22A	Replic. 56-19A proc.	1.6	0.6	5.8	8.1	na	
56-22B	Replic. 56-19B proc.	-0.8	-0.2	1	1	na	
56-23	Replic. 56-19B proc.	-0.3	1.5	0.2	2.1	1.5	4.2
56-24	Replic. 56-19B proc.	-0.2, 1.0	2.2, 2.1	1.3, 3.4	7.5, 4.5	3.6, 6.4	8.0,8.9
56-26	Reprod 56-22B at 2x scale	-0.2, 2.0	2.4, 3.0	0.6, 4.3	3.0, 6.4	3.8, 10.3	7.5,14.7
56-27	Mod 52-70 proc. to tighten wall	na, 0.7	1.1, 0.6	na, 1.5	2.2, 3.9	4.2, 6.7	5.9,10.2
56-28	Mod 52-70 proc. to tighten wall	na	2.6	na	6.6	11.3	16.8
56-29	Mod 52-70 proc. to tighten wall	na, 0.3	0.9, 0.6	na, 0.7	1.0, 1.2	2.1, 2.4	5.2,3.9
56-34	56-22B proc.; 75% DCOIT	6.6	15.3	19.2	16.8	20.5	23.7
56-35	Thicker wall, reduced core	0.5	0.8	1	1.9	4.9	7
56-38A	Proc. mod, thicker wall	1.5	2.5	3.1	4.6	9.7	13
56-38B	Proc. mod, thicker wall	1.3	1.8	2.1	4	11.8	9.4
56-43	Replic. 56-19B proc.	8.1	15.4	17.9	21.2	23.2	28.2
56-44	Replic. 56-19B proc.	1.4	3.4	5.2	7.9	10.4	20.7
56-59	Replic. 56-43 proc.	3	5.5	7.1	10.8	13.6	16.3
56-58	Replic. 56-44 proc.	1.9	3.1	4.7	12	10.6	11.7
		NOTE: Two values are shown for samples analyzed a second time.					
Amino-Ureaformaldehyde batches							
56-40	Conventional process	0.7	0.6	0.8	1.1	0.9	2.4
56-41	"	2.5	2.8	2.9	3.1	3.1	3.8
56-42	Thicker wall, reduced core	0.4	0.4	0.6	0.5	2.1	1.7
56-45	Reprod. M56-41 at 2x scale	0.4	0.5	0.5	1	1.9	1.5
56-48	Process modification	0.8	0.9	1.7	1.4	1.1	1.9
56-54	Conventional process	0.4	0.4	0.8	1.6	0.8	1.6
56-55	Increased core, thinner wall	2.8	3	3.1	5.3	3.1	3.9
56-56	Process mod, less cure	1.9	1.9	2.4	3.8	2.5	3.4
56-61	Process modification	3.7	4.5	4.8	4.5	4.9	6.2

Table 3. Room temperature xylene extraction data from Microtek.

In-can stability:

Two separate analyses were used to evaluate this property.

- Airless Spray Impact on Capsules: Rohm and Haas sampled the sprayed ablative coating sample (discussed above) in liquid form. Capsules were filtered out and the remaining liquid was quantitatively analyzed for DCOIT. Only 5% of the theoretical original DCOIT loading was detected, thus indicating the extraction into the liquid paint is far less than would be predicted by extraction into xylene alone. Note that the xylene extraction test (results presented in Table 3) is a more severe challenge when compared to the protocol described here. This is not a standardized test, and this is a single data point, but considering the elapsed time between the generation of the sample and the analysis (months), the quantity of biocide prematurely released into the liquid paint was low.
- Jotun A/S storage stability analysis: The liquid paint-capsule combinations used for the field panel evaluation were used by Jotun A/S to conduct a company-proprietary storage stability mini-study. Capsules were added at the same relative loading as for panel preparation. Following capsule addition, separation, settling, viscosity, and grind (company proprietary protocols) were quantified (Table 4). All of the results indicate stable/normal paint behavior, and are consistent with previous results (conducted under pre-ESTCP Program funding) for this product.

Storage Stability of Ablative Jotun Coating with Capsules							
Formulation	Jotun Ablative Coating with M49-34 (3354-03) encapsulated DCOIT						
Date of reading	4/8/2005	5/10/2005		8/7/2005		10/7/2005	
Months	0	1	1	3	3	6	6
Temperature	Start	23°C	52°C	23°C	52°C	23°C	52°C
Sample no.		1A	1B	2A	2B	3A	3B
Separation		15%	15%	15%	25%	15%	25%
Settling		soft	soft	soft	soft	soft	soft
Stormer (KU)	88	83	96	94	117	91	106
Viscosity (cP)	460	490	640	430	720	480	750

Table 4. Results from liquid paint storage stability mini-study. Capsules from batch M49-34 formulated into Jotun copper ablative coating.

Environmental considerations:

Suitable alternative solvents to SAS 310 were identified (mineral oil, Exxon 100, Exxon 150, mineral spirits, C13 alkyl benzene), and properties of successful runs met the established key performance criteria. Solvent-less capsules and very high core loadings are possible when amino urea formaldehyde wall materials are used (Table 2, all batches except 56-40, 56-41, and 56-54). Solvent-free cores eliminate concerns over TSCA import/export restrictions and maximize capsule and therefore coating loading potential.

Dry coating – capsule compatibility:

Based on results obtained under ONR-MANTECH funding, PVA-phenolic capsules do not contribute to coating cracking tendency, do not affect polishing rate or copper release rate, and

do not agglomerate during cure. Due to time and funding constraints, a parallel thorough assessment of these properties was not completed for AUF capsules produced under this effort. However, for one capsule/coating combination, coating dried films had acceptable physical characteristics (see Table 4) in follow-on testing (Jotun proprietary techniques). NOTE: viscosities under 750 cP indicate a sprayble coating.

Commercial viability:

The reaction conditions and process controls are extremely important in order to achieve the desired capsule properties. Batch to batch reproducibility as indicated by xylene extraction rates improved over time. Compare xylene extraction data for batches 56-19A, 56-21A, 56-22A (Table 3).

Capsules of the appropriate size (diameter) and size distribution were produced, and could be air dried without added drying aids.

Microtek reported successful batch size scale up to 250-500g for capsule chemistries similar to those covered by this report. Successful scale up includes maintenance of particle diameter and size distribution, no impact on xylene extraction, and successful drying to a fine powder (Microtek company proprietary data. Work conducted under commercialization agreement with Rohm and Haas).

Rohm and Haas has initiated a robust commercialization effort for microencapsulated DCOIT with, at a minimum, Microtek as the supplier of microencapsulated DCOIT. The details of the commercialization effort cannot be included in this report, and are considered sensitive information. Rohm and Haas and their commercial partners will assume technical risk associated with producibility in their full scale commercialization effort.

Performance advantage:

During the 12-month field panel study, no significant accumulations of hard fouling were observed, and only slight variations in slime accumulation were noted. (See section 2 – Field Exposure for more details). The commercial reference coating (with no DCOIT) accumulated more slime than capsule-containing and DCOIT-containing coatings. Microencapsulation reduced DCOIT release rate significantly (see Field Exposure and Release Rate sections) and enhanced performance.

2) Field Exposure

Static exposure and *Dynamic exposure*

Panels were exposed at Battelle Memorial Labs in Daytona, FL for 12 months. Over that period, no significant fouling and no hard fouling was observed on panels (Figure 8). Unlike the previous 3-year study, the quantity of DCOIT lost from both the static and dynamic panels containing microencapsulated DCOIT was much lower than from the panels containing unencapsulated (or neat) DCOIT (Table 5). In addition, panels with encapsulated DCOIT show lower average biocide release over time, and show similar AF efficacy as panels with unencapsulated DCOIT. These results match expectations. However, these results do not eliminate the possibility that at some later point in time capsule-containing coatings might

release DCOIT at a higher rate than non-capsule-containing coatings. In this test, this phenomenon did not occur within the first 12 months of exposure.

Each of the sampling techniques (see section 4.1.1 Section 2) used to quantify DCOIT loss from field-exposed films produced different results, but the relative quantities of retained DCOIT, whether encapsulated or unencapsulated, were about the same. Reproducibility was highest with the second technique. The most troubling result was the inability to explain the particularly high starting concentration of DCOIT in all of the unexposed panels. The disparity is either due to a coating formulation error or due to an error in sampling technique. Despite the lack of suitable explanation for this observation, we were still able to calculate a relative DCOIT loss by weight, and, according to Rohm and Haas, DCOIT loss rates from capsule-containing coatings were lower than what Rohm and Haas would expect from commercial antifouling formulations containing unencapsulated DCOIT.

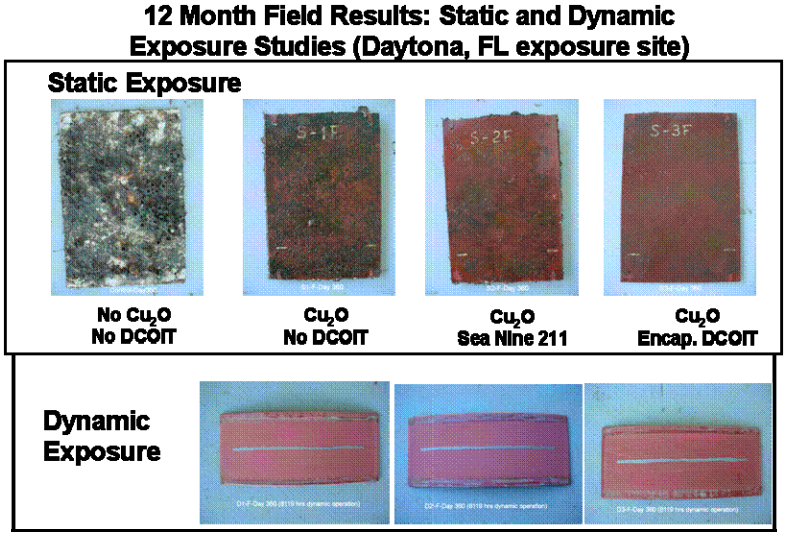

Figure 8. Representative photos of field-exposed panels. 12-month exposure images shown.

DCOIT Loss over 12-month Field Exposure Evaluation			
Test	Sample	% DCOIT Lost After 12 Months	Average Release Rate over 12 Months ($\mu g\ cm^{-2}d^{-1}$)
Static	SeaNine 211	42.0	1.3
	Encapsulated DCOIT	11.8	0.6
Dynamic	SeaNine 211	54.9	1.2
	Encapsulated DCOIT	11.6	0.5

Table 5. Results of quantitative DCOIT analysis on field-exposed test panels coated with AF systems containing either encapsulated (batch 49-34) or unencapsulated DCOIT.

3) Capsule Property Studies

Over 3-dozen small batches of microcapsules (100-150 grams) were produced to systematically analyze the impact of formulation changes on capsule properties and function (Table 2). As described above (Section 4.1.1 subsection 3), xylene and seawater extraction studies were used to assess impact of capsule properties on capsule function.

An overview analysis of the data set indicates the following:

- Wall thickness – increasing capsule with thickness, whether amino urea formaldehyde or PVA phenolic, reduced biocide release. This was true for:
    - xylene extraction
        - PVA Phenolic – Table 3, Batch 56-19 compared with batch 56-38A
        - AUF – Table 3, Batch 56-40 compared with batch 56-55
    - seawater extraction
        - PVA Phenolic – Figure 9, Batches 56-70 vs 56-40
        - AUF – Figure 10, batches 56-40 vs 56-55
- Reproducibility –
    - Tightly-controlled reaction conditions were especially critical in the production of PVA-Phenolic capsules. This is evidenced by higher variability in replicate production batches of 56-19A and B.
    - Amino-urea formaldehyde chemistry produces more stable capsules, and although control of reaction conditions was still important, reproducibility was more easily achieved as evidenced by lower variability in xylene extraction studies (Table 3).
- Core loading –
    - It was not possible to encapsulate high core loadings of DCOIT with PVA-Phenolic wall chemistry. Maximum core loading successfully achieved was about 45 weight percent. Batches 56-19B and 56-20B has DCOIT contents of about 40 weight percent whereas batch 56-34, with a much higher core loading, has a high xylene extraction rate which is indicative of “leaky” capsules with compromised wall integrity (Tables 2 and 3).
    - It was possible to produce capsules with very high DCOIT core loadings (no solvent) with amino-urea formaldehyde wall chemistry. Maximum core loading successfully achieved was just under 90 weight percent (Table 2). Extraction rates in xylene were, on average, lower than PVA Phenolic. As with PVA Phenolic capsules, extraction rates of AUF capsules were a function of wall properties (Tables 2 and 3, batches 56-48, 55, 56, and 61).
- Core solvent for biocide –
    - SAS 310 was replaced with the following solvents: Exxon 100, Exxon 150, mineral spirits, and mineral oil. A subset of capsule batches with these core solvents met or exceeded key performance criteria. Extraction rates in xylene varied, but not significantly in some cases (Tables 2 and 3 batches 56-22A, 56-23, and 56-24 respectively).
    - In some cases (Exxon 100 and Mineral Oil), seawater extraction studies indicate little impact of core solvent on DCOIT release when compared to SAS 310 (Figure 9).
    - None of the alternative solvents are subject to import/export restrictions.

- Capsule diameter –

  Historical capsule batches averaged about 30-40 µm in diameter. A target of 20µm average capsule was achieved, with a maximum particle size of 30 µm (Table 2 – most batches).

- Sprayability –
  - There was no evidence of capsule breakage or cracking during formulation or airless spray application (Section 4.1.1 section 3) with downselect batches of capsules (see also Figure7 and Section 4.1.2 – Wall Integrity and Film Formation).

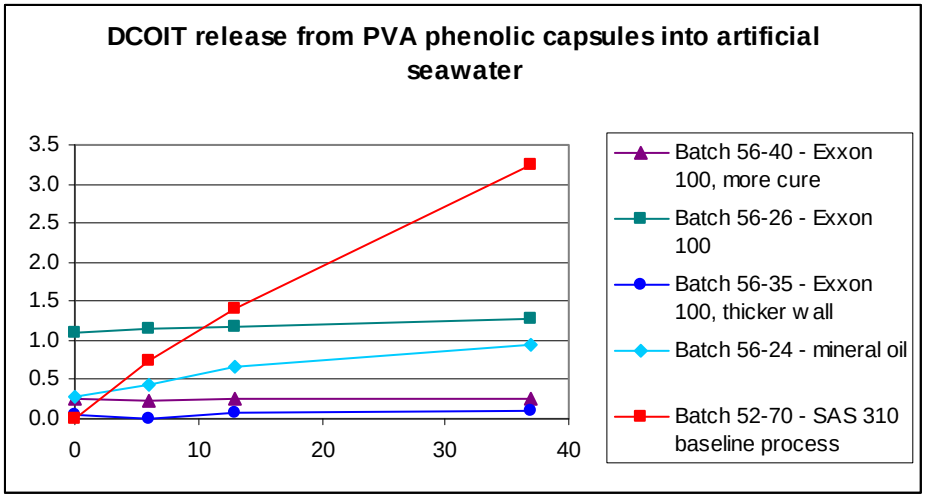

Figure 9. DCOIT release from PVA Phenolic capsules into artificial seawater. Release varies with core material and wall thickness.

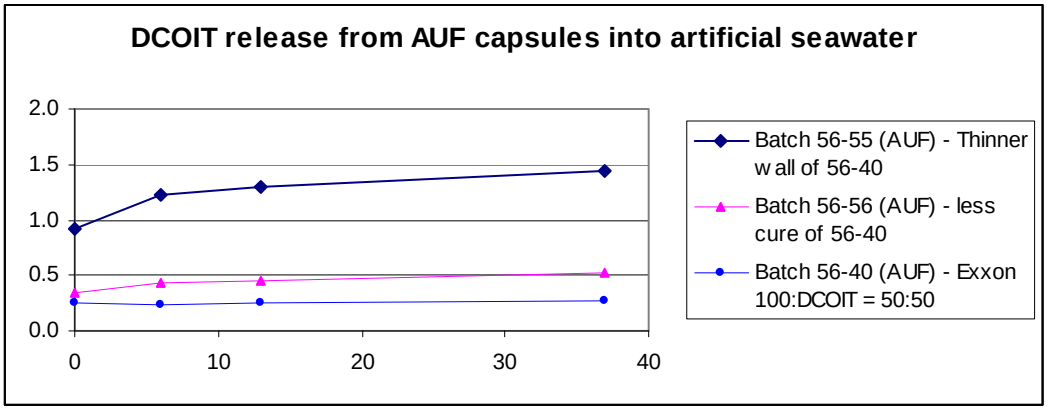

Figure 10. DCOIT release from Amino Urea Formaldehyde capsules into artificial seawater. Release varies with wall thickness and cure.

Storage stability –

- As described above, the xylene extraction tests and the in-can spray study gave an indication of storage stability. Further analysis indicates that the amino urea

formaldehyde shell wall chemistry retarded DCOIT loss over PVA-Phenolic chemistry (Fig. 11).

- Capsules with low xylene but high seawater extraction rates were the most desirable since they would retain the core payload while in the can (prior to application), yet release DCOIT at an effective rate from the coating.
- Storage stability involves more than just premature core biocide release from capsules (e.g. capsule wall integrity, coating viscosity, pigment settling, etc.). Storage stability would need to be more fully addressed a commercialization effort, and would likely be addressed by both the microcapsule and coating manufacturers using proprietary techniques.

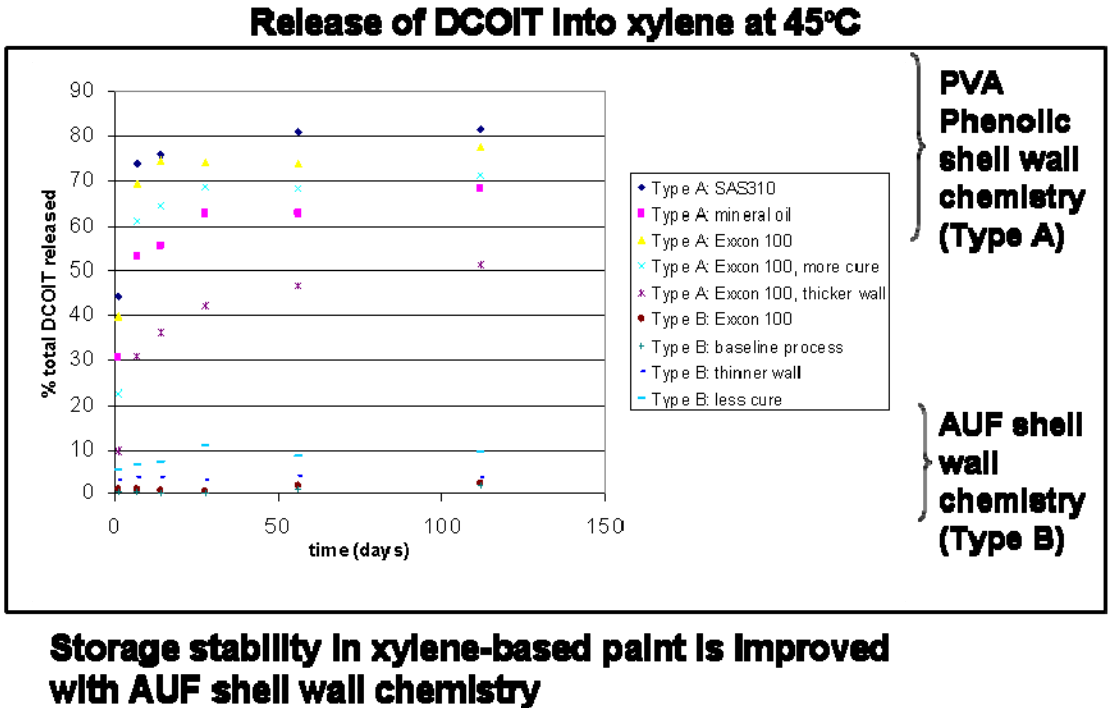

Figure 11. DCOIT release from capsules into xylene - two different wall chemistries. Storage stability in xylene-based paint is improved with amino urea formaldehyde shell wall chemistry. (Note: Type A shell wall chemistry = PVA Phenolic, Type B shell wall chemistry = AUF)

4) Release Rate Analysis

DCOIT release rates were determined based on an adaptation of the draft ASTM Z9489Z organic biocide release rate method (reduced number of sampling points and increased rotation time). DCOIT release rate from all capsule-containing coatings were much lower and approached zero order when compared to unencapsulated DCOIT (Fig. 12). Release rates from capsule-containing coatings only (Fig. 13) indicate DCOIT release rates from several capsule-containing coatings approached zero order, especially if the data on day 28 are ignored. NOTE: Systematic shifts in release rate data (such as the day 28 data in Fig. 13) from multiple coatings tested at the same time in the same laboratory have

been observed in the past (personal communication, Charlie Willis. There is no technical explanation for this phenomenon at this time.)

Extending the rotation time to 5 hours in order to maximize the cumulative release of DCOIT did not always result in sufficient DCOIT release to meet method limits of detection and quantitation. Despite that, comparing the overall set of capsule release rates indicates a logical impact of capsule properties on DCOIT release (Fig 13). For example, lower DCOIT release rate from AUF wall chemistry compared to PVA Phenolic wall chemistry. Also, we expected coatings with higher capsule loadings to result in higher DCOIT release rates. And, we expected higher release rates from the base process capsules (M49-34) than the more optimized PVA Phenolic capsules (M56-24).

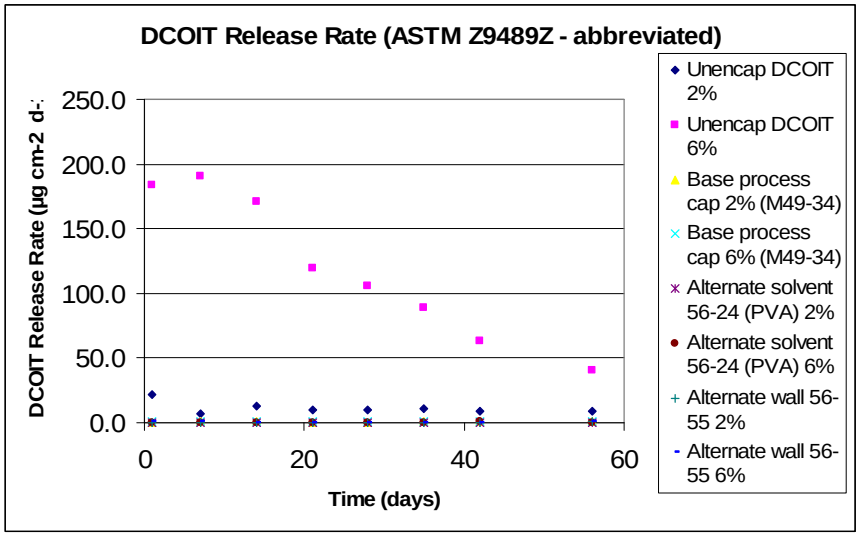

Figure 12. DCOIT release rate from copper ablative coating – some containing encapsulated DCOIT and coatings containing unencapsulated DCOIT; 2 different loadings (2% and 6%); 2 different chemistries (PVA Phenolic (base process and optimized) and AUF (alternate wall)).

The DCOIT release rate test was originally scheduled to run for 180-days, but was cut short for the following reasons: 1) 56-days of data were enough to indicate trends, 2) many of the data points were close to the method LOD and LOQ, and 3) Rohm and Haas suggested that capsules with a slightly higher release rate would be desirable for commercially viable capsule-containing coatings as indicated by batches of further optimized DCOIT capsules which had already been produced by Rohm and Haas and Microtek under their commercialization agreement. In addition, the group felt that the money saved by ending this test early would best serve the overall program when put towards an assessment of the impact of copper microencapsulation on copper release rates. NOTE: the copper release rate evaluation is in progress, and not included in this report. Results will be submitted as an addendum to this report as late as 3rd Q FY07 (assuming the test runs the full 180 days).

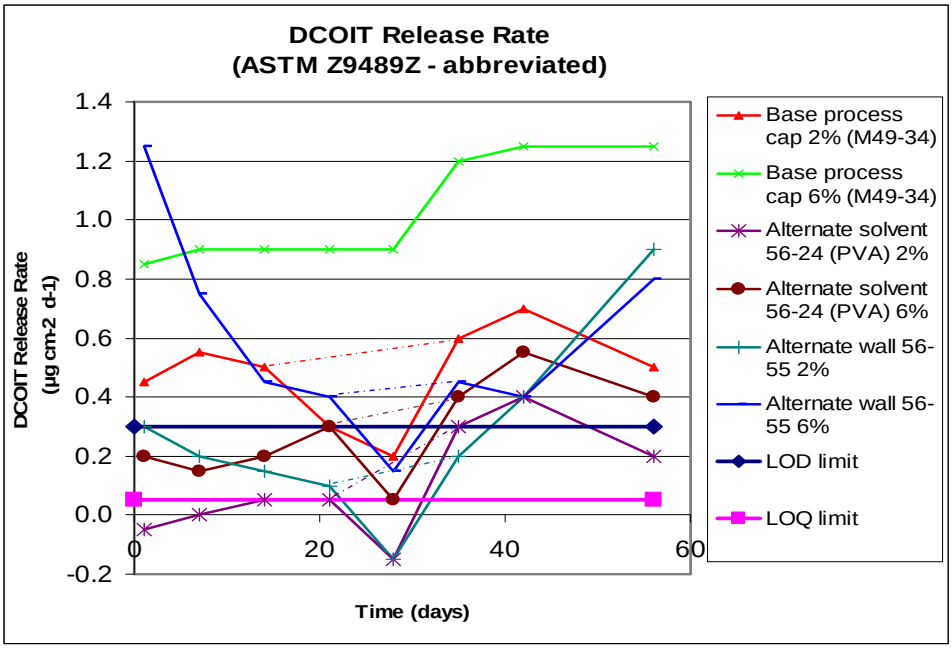

Figure 13. DCOIT release rate from copper ablative coating containing encapsulated DCOIT; 2 different loadings (2% and 6%); 2 different chemistries (PVA Phenolic – 56-24 (optimized) and AUF – 56-55).

We now have two release rate data sets for DCOIT release from AF coatings containing capsules with PVA Phenolic chemistry. Both data sets indicate the capsules significantly reduce DCOIT release rate, and that release rate is near zero order. We now have one data set that indicates AUF capsules in an AF coating further reduce DCOIT release rate, at least over the first 40 days.

4.1.3 Conclusions Based on Results of New Tasks

The experimental design was executed as planned. The cumulative results demonstrate the following:

- Microcapsules with DCOIT cores that meet all of the identified key performance parameters can be produced with at least two wall chemistries.
- Coatings containing microencapsulated biocide retain more DCOIT over long periods of time than coatings that are formulated with free DCOIT. This is true in both the laboratory and in the field.
- Microencapsulated DCOIT, when incorporated into commercially relevant antifouling coating systems, enhances overall coating performance.
- DCOIT release rates into seawater and xylene can be controlled through microencapsulation.
- Both laboratory release rate studies and field biocide loss studies produce predictable results based on capsule properties and coating formulation.
- Microencapsulation allows high levels of DCOIT to be loaded into coatings without negatively impacting liquid or cured coating properties.

The sum of what was learned met or exceeded the goals of re-scoped ESTCP Program task plan. This worked was successful in filling the existing data gaps, improving technical maturity, and improving the understanding of biocide release from capsules and from coatings containing encapsulated biocide. Together with the results from previously-funded efforts, the progress was sufficiently significant for Rohm and Haas and Microtek Laboratories, Inc. to launch a full-scale commercialization effort independent of ESTCP funding. Rohm and Haas and Microtek will take on many of the high risk scale-up issues such as reproducibility of capsule batches, bringing together the proper capsule properties to the end-use coating technology (especially among multiple companies), registration concerns, and related production environment concerns.

Their commercialization effort, when successful, will not necessarily produce a capsule-containing material suitable for DoD end use. As mentioned in section 1.4, DoD vessels have unique operational profiles and technical needs, and the US environmental rules are particularly stringent when compared to the global commercial shipping industry. Therefore, assuming Rohm and Haas and Microtek are successful in their commercialization efforts, a follow-on ESTCP funded effort would increase the potential that end products that meet or exceed the DoD's unique needs would be produced (e.g. compliance with the military performance specifications, US environmental policy, and UNDS requirements).

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Appendix A – Field test – panel preparation details

Static panel preparation: PVC panels with holes in each corner, 1 cm from the edges, were washed and cleaned with xylene. One coat of epoxy primer was applied on each side (Safeguard Universal ES, 50 µm). Three coats of antifouling were applied on the front side of the panels (3*100 µm), except for 6 panels that only had 1 coat (1*100 µm) to mimic the 3-year test panels described above (See Table A-1). One day drying was allowed between each coat, except for the third coat of antifouling that was applied after

Paint ID	Paint Name	Biocides*	DCOIT loading (wt%) Wet paint	Dry paint	Panel preparation**
3354-01	Commercial Jotun Ablative	Cu_2O	0	0	1 coat AC + 3 coats AF
3354-02	Commercial Ablative + DCOIT	Cu_2O + Sea-Nine 211	2.2	2.7	1 coat AC + 3 coats AF
3354-03	Commercial Ablative + ME DCOIT batch M49-34	Cu_2O + M49-34	2.2	2.7	1 coat AC + 3 coats AF
3354-04	Commercial Ablatiave + ME DCOIT batch M49-34	Cu_2O + M49-34	2.2	2.7	1 coat AC + 1 coat AF

*Sea-Nine 211 contained 30wt% DCOIT and M49-34 contained 35.5 wt% DCOIT.

**The steel curved panels were coated with 2 coats of AC, flat PVC panels with one

Table A-1. Panels for field study - 12-month biocide loss with time.

3 days of drying. The panel ID codes were applied with a white non-polishing antifouling. The paints were applied on 4 sets of panels, three sets of panels coated with 3 coats of AF, and one set of panels coated with one coat of AF. Each panel set contained 6 panels: Panel A was not exposed, and the remaining 5 (B through F) exposed for 2, 4, 6, 9 and 12 months. The panels were exposed back-to-back in East/West directions, suspended from floating rafts at 2 ft below the surface. The B-panels were exposed back-to-back to each other, and the same went for C, D, E and F panels.

Dynamic panel preparation: The steel panels were sandblasted to Sa 2.5. The panel edges were dipped in epoxy primer (thinned paint) and two coats of epoxy were applied on each side (1*200 µm Jotamastic 87 Alu and 1*50 µm Safeguard Universal ES Grey). Three coats of antifouling were applied on the front side (outer curved surface) of the panels (3*100 µm), except for 6 panels that only had 1 coat of paint (1*100 µm) per above. The drying time and panel ID codes were applied as for the static panels. The panels were attached to a drum with “bands” that held

the panels lengthwise at the top and bottom. The drum was positioned vertically in the water column, and spun continuously on its axis at a peripheral speed of about 18 knots.

The panels were exposed on 6 December 2004. The panels marked:

- A were not exposed – they are the pre-exposure "controls"
- B were removed for analysis on 31 Jan 05 after approximately 2 months of exposure
- C after 4 months
- D after 6 months
- E after 9 months
- F after 12 months

After each exposure period, digital photos were taken and an assessment of fouling level was performed. After removal from the test site, the panels were dried and shipped to Rohm and Haas for quantitative analysis.